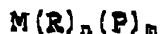


CLAIMS

1. A homogeneous process for the preparation of reactive sol-gel porous materials either chemically or physically doped with stable organic nitroxyl radicals, comprising the steps of:

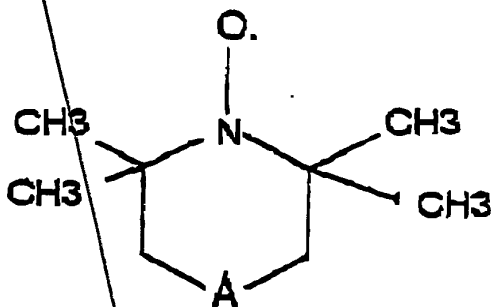
a) copolymerizing a solution including:

at least one monomer precursor selected from the group including metal and semi-metal alkoxides, metal esters or semi-metal esters, of the general formula



wherein M is a metal or a semimetal, R is an hydrolyzable substituent, P is a non-polymerizable group, n is an integer of 1 to 6, and m is an integer of 0 to 6,

a dopant consisting of a stable di-tertiary-alkyl nitroxyl radical or a precursor thereof of formula



wherein A represents a chain of two or three carbon atoms, one or two of said carbon atoms being eventually substituted by one oxygen or nitrogen atom,

a solvent including H₂O and a co-solvent generally selected from aliphatic alcohols;

an acid or base to catalyse the processes of sol-gel hydrolysis and copolymerization; and

one or more additives selected from those known to be useful in the preparation of porous materials

to form a gel containing said dopant trapped therein;

b) evaporating said solvent;

c) drying said gel;

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d) coating said gel on a mesoporous inorganic support; and

e) drying said mesoporous material coated with said sol-gel.

2. The process according to claim 1, wherein M is Si, Ti, Pb or Al and R is an alkoxy or arylalkoxy group.

3. The process according to claim 1 or 2, wherein said non-hydrolyzable substituent is H, an alkyl, aryl or fluoroalkyl group or an aminoalkyl group.

4. The process according to ^{claim 1} ~~any one of the preceding claims~~, wherein said step c) of drying the gel is a liophilisation carried out at a pressure lower than 70 mm Hg and preferably 15 mm Hg, to obtain a mesoporous aerogel powder.

5. The process according to ^{claim 1} ~~any one of the preceding claims~~, wherein said step c) of drying the gel is a mild heat treatment carried out at an atmospheric pressure and a temperature lower than 100° C, and preferably at 45° C.

6. The process according to claim 1, wherein said nitroxyl radical is added to said solution along with said monomer precursor in a one-step procedure.

7. The process according to claim 1, wherein in a two-step procedure, first said monomer precursor is hydrolyzed in part with water in the presence of an acid and then said nitroxyl radical is added to this solution, to obtain a porous sol-gel polymeric oxide with a fractal macromolecular structure.

8. The process according to ^{claim 1} ~~any one of the preceding claims~~, wherein said nitroxyl radical is 4-oxy-TEMPO and said monomer precursor is 3-aminopropyl-trimethoxysilane to obtain a catalytic material containing chemically linked radicals.

9. The process according to claim 8, wherein said radical is tethered to said monomer precursor through reductive amination by stirring for three hours a solution of 4-oxo-TEMPO in methanol with a slight excess

of 3-aminopropyl-trimethoxysilane, and reducing the thus formed imine with NaBH_4CN .

10. The process according to any one of claims 1 to 7, wherein said nitroxyl radical is TEMPO or a precursor thereof and said radical is physically entrapped within a sol-gel matrix adding a solution thereof in methanol to said precursor following either said one- or two-step procedure as claimed in claim 6 or 7.

11. The process according to claim 1, wherein said catalytic porous materials are in the shape of powders, films, monoliths, or fibers.

12. Use of a doped porous material obtained with a process as claimed in any one of claims 1 to 11, to catalytically mediate a liquid-phase oxidative conversion of primary and secondary alcohols into carbonyl or carboxyl derivatives in the presence of a primary oxidant.

13. A process for the liquid-phase oxidative conversion of a substrate of a primary or secondary alcohol into a carbonyl or carboxyl derivative thereof, characterized in that said oxidative conversion is carried out in the presence of a doped catalytic material as defined in any one of claims 1 to 11, and in the presence of a primary oxidant effective in selective alcohol oxidations mediated by nitroxyl radicals.

14. A process according to claim 13, wherein said liquid phase is an organic solvent, a biphasic organic solvent-water system, or water and said primary oxidant is NaOCl , NaOBr , HNO_3 , CuCl/O_2 , $\text{K}_3\text{Fe}(\text{CN})_6$, or NO_2 .

15. A process according to claim 13 or 14, wherein said alcohol substrate is an alkyl alcohol, an aryl alcohol, a steroid alcohol, an allylic alcohol, a terpenoid alcohol or retinol and it is oxidated in a biphasic reaction system $\text{CH}_2\text{Cl}_2\text{-H}_2\text{O}$, said primary oxidant is aqueous alkaline NaOCl and said catalytic material is prepared according to claim 8 or 9 and it is added to the reaction system under stirring.

16. A process according to claim 13 or 14, wherein said alcohol substrate is a monomer or an oligomeric carbohydrate protected at the anomeric center, said solvent is water, said oxidant is alkaline NaOCl or NaOCl in the presence of a catalytic amount of NaBr, and said catalytic material added to the reaction solution is one as claimed in anyone of claims 8, 9 or 10.

17. A process according to claim 16, wherein said catalytic material is in the form of pumice stones coated with a sol-gel film doped with said nitroxyl radicals as claimed in anyone of claims 1 to 10 and said carbohydrate is a water soluble polymer.

18. The catalytic material doped with a chemically linked nitroxyl radical obtained with a process as claimed in anyone of claims 8 or 9.

add B1x

add B6/p

add B3

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